Inorg. Chem. **2006**, *45*, 5393–5398

Inorganic Chemistry
Article

Two New Hybrid Organic/Inorganic Copper(II)–Oxovanadate(V) Diphosphonates: $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]\cdot H_2O$ and $[Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$. Synthesis, Structure, and Magnetic Properties

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Received January 26, 2006

Two new hybrid organic/inorganic copper oxovanadium diphosphonates $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]\cdot H_2O$ (**1**) and $[(Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$ (**2**) have been obtained by hydrothermal synthesis. The compounds are monoclinic, and they crystallize in the space group $P2_1/n$ with cell parameters of $a = 11.788(2)$ Å, $b = 17.887(3)$ Å, $c = 14.158(2)$ Å, and $\beta = 93.99(0)°$ and in the space group $C2/c$ with cell parameters of $a = 11.025(1)$ Å, $b = 18.664(2)$ Å, $c = 15.054(2)$ Å, and $\beta = 90.06(0)°$, respectively. Both compounds present two-dimensional frameworks built up from infinite chains of corner-sharing vanadium tetrahedra and diphosphonate groups connected by copper tetramers for (**1**) and copper dimers for (**2**). The remarkable feature of (**2**) is the encapsulation of propane molecules, stabilized by strong hydrogen bonding between the layers. The magnetic properties of the compounds have been investigated showing antiferromagnetic coupling with $T_{max} = 64$ K for (**1**) and Curie-like paramagnetic behavior for (**2**).

1. Introduction

The vanadium phosphate system has been widely investigated since the discovery of $(VO)_2P_2O_7$ [1] and its catalytic properties in the selective air oxidation of butane to make maleic anhydride. Hydrothermal treatment has proven its great efficiency for obtaining new structural arrangements. Under these synthetic conditions, three oxidation states are accessible for the vanadium atoms (5+, 4+, and 3+) which lead to a great variety of coordination polyhedra: tetrahedra (V^{5+}), square pyramids and distorted octahedra (V^{5+}, V^{4+}), trigonal bipyramid (V^{4+}), and regular octahedra (V^{3+}). In addition, the phosphate species may be present in the solids with 0, 1, or 2 terminal oxygen atoms, protonated or not, and even in combination with the different groups. The vanadium and phosphorus polyhedra exhibit variable connectivites including corner-, edge-, and face-sharing with homo- and heterocondensation.[2]

Numerous compounds have been isolated with inorganic and organic structure-directing subunits; the last one corresponds to organoamines generally introduced in the structures as cationic components, generating porous materials.[3−18]

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10.1021/ic060152g CCC: $33.50

More recently the organic part has been incorporated by direct replacement of the phosphate group by organophosphate;[19−22] the size variation and the nature of the organic part was used to modify the framework.

Extension to chelating ligands such as diphosphonate,[23−30] phosphonate−carboxylate,[31,32] and phosphonate−pyridine[33] groups, is of interest in various systems because of the separation of two or more functional groups connecting the metal centers by the organic part. This organic moiety may act not only as a structural modifier but also as a spacing agent (for example methylene to octylene in diphosphonate compounds).

We report herein the synthesis, structure, and magnetic properties of the two-dimensional compounds $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]\cdot H_2O$ (**1**) and $[Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$ (**2**). Compounds containing Cu^{II} atoms coordinated by diamines have been recently investigated because of the structure-directing role of the copper centers, which can connect the metal atoms and phosphates or phosphonates with the organonitrogen ligand permitting $\pi-\pi$ stacking. This type of material has also shown interesting magnetic properties because of the presence of the copper centers.[34−38]

Table 1. Selected Crystallographic Data for $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]\cdot H_2O$ (**1**) and $[Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$ (**2**)

	1	**2**
empirical formula	$C_{25}H_{22}Cu_2N_4O_{13}P_2V_2$	$C_{30}H_{30}Cu_2N_4O_{11}P_2V_2$
fw	877.38	913.48
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	11.7880(17)	11.0247(13)
b (Å)	17.887(3)	18.664(2)
c (Å)	14.158(2)	15.0544(17)
α (deg)	90	90
β (deg)	93.988(2)	90.063(2)
γ (deg)	90	90
V (Å^3)	2978.0(8)	3097.7(6)
Z	4	4
density (calcd)	1.952 g/cm^3	1.959 g/cm^3
abs coeff	2.200 mm^{-1}	2.115 mm^{-1}
data/params	6773/450	2725/233
R_1 (F_o) ($I > 2\sigma(I)$)	0.0473	0.0444
R_2 (F_o)	0.1041	0.1237

2. Experimental Section

2.1. Synthesis. The reagents used for the synthesis of both compounds were V_2O_5 (Aldrich), $Cu(NO_3)_2\cdot 3H_2O$ (Merck), Zn (Fluka), 1,10-phenantroline (Aldrich), methylenediphosphonic acid as trisodium salt tetrahydrate (Aldrich), and propylenediphosphonic acid (Alfa Aesar).

Hydrothermal reactions were carried out in a Teflon acid digestion bomb (23 mL, Parr Instruments) under autogenous pressure at 120 °C for 72 h. The reaction vessels were then cooled to room temperature, the resulting products were filtered off, washed with distilled water, and dried under vacuum in a desiccator. Compounds (**1**) and (**2**) were obtained only as minority phases. Subsequent attempts involving a different synthesis route (a two-step reaction with the dissolution of V_2O_5 with diphosphonic acid first, followed by the transfer of the solution into the acid digestion bomb for 2 days of heating, after addition of the copper nitrate and the 1,10-phenantroline) did not improve the yield of the reaction. Thus, optimal conditions to obtain pure crystalline phases have been unsuccessful so far. Visual examinations under an optical microscope allowed us to separate crystals suitable for single-crystal X-ray diffraction studies, and a sufficient amount to perform physical characterizations.

Synthesis of $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]$ H_2O (1). Blue rod-shaped crystals of (**1**) were obtained by the hydrothermal treatment of the starting mixture: V_2O_5 (0.0765 g), $Cu(NO_3)_2\cdot 3H_2O$ (0.203 g), 1,10-phenantroline (0.084 g), methylenediphosphonic acid (0.132 g), and H_2O (5 mL) in a molar ratio of 1:2:1:1:662. The pH values measured before and after the reaction were 6 and 3, respectively.

Synthesis of $[Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$ (2). Blue prismatic crystals of (**2**) were obtained by a hydrothermal treatment of the starting mixture V_2O_5 (0.0765 g), $Cu(NO_3)_2\cdot 3H_2O$ (0.203 g), Zn (0.053 g), 1,10-phenantroline (0.084 g), propylenediphosphonic acid (0.089 g), and H_2O (5 mL) in a molar ratio of 1:2:2:1:1:662. The pH values measured before and after the reaction were 3 and 5, respectively.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)]\cdot H_2O$ (**1**) and $[(Cuphen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)]\cdot C_3H_8$ (**2**)

1											
Cu1						Cu2					
O1	1.934(2)					O4	1.948(2)				
O6	1.952(2)	97.4(1)				O3	1.981(2)	92.0(1)			
N1	1.992(3)	164.2(1)	90.4(1)			N3	2.004(3)	91.5(1)	166.9(1)		
N2	2.013(3)	87.4(1)	166.8(1)	82.2(1)		N4	2.013(3)	163.4(1)	91.7(1)	81.5(1)	
O1W	2.247(3)	94.0(1)	99.6(1)	98.2(1)	92.3(1)	O3	2.280(2)	90.7(1)	81.0(1)	111.6(1)	105.8(1)
V1						V2					
O8	1.606(3)					O10	1.607(3)				
O7	1.613(3)	108.0(2)				O11	1.621(3)	109.4(2)			
O9	1.791(3)	112.8(1)	109.1(1)			O9	1.798(3)	110.1(1)	110.2(1)		
O2	1.872(2)	108.0(1)	110.0(1)	109.0(1)		O5	1.866(2)	108.7(1)	106.6(1)	111.7(1)	
P1						P2					
O1	1.501(3)					O6	1.505(2)				
O3	1.518(2)	112.0(1)				O4	1.511(2)	114.3(1)			
O2	1.535(2)	111.1(1)	109.1(1)			O5	1.545(2)	109.0(1)	109.3(1)		
C25	1.798(3)	108.9(2)	107.7(1)	108.0(1)		C25	1.799(3)	110.2(1)	108.0(1)	108.5(1)	
2											
Cu1						V1					
O61	1.905(3)					O3	1.605(4)				
O5	1.926(3)	97.5(1)				O1	1.640(3)	108.1(2)			
N2	2.005(4)	167.0(1	90.2(1)			O2	1.777(1)	109.8(2)	112.6(2)		
N1	2.029(4)	90.4(1)	171.2(1)	81.3(1)		O4	1.854(3)	107.8(2)	108.5(2)	109.8(2)	
O1	2.432(4)	95.3(1)	95.3(1)	94.3(1)	87.5(1)						
P1											
O6	1.501(3)										
O5	1.511(3)	115.6(2)									
O4	1.556(4)	110.4(2)	110.3(2)								
C13	1.788(4)	105.2(2)	108.6(2)	106.2(2)							

2.2. X-ray Diffraction. The crystal structures of (**1**) and (**2**) were determined by single-crystal X-ray diffraction. The experiments were performed at room temperature using a Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data collection was performed in the $\omega-\phi$ scanning mode using 0.3° of separation between frames and 20 s per frame. The crystal to detector distance was 62.8 mm. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was performed using SADABS.[39] Data integration was made using SAINT.[40] The structures were solved by means of direct methods using SHELXS97,[41a] completed by Fourier difference synthesis and refined until convergence using SHELXL97[41b] in the SHELXTL package.[41] For additional data collection and refinement details, see Table 1. Bond distances and angles are presented in Table 2.

2.3. Magnetization Measurement. Zero-field cooled magnetic susceptibility was measured over the temperature range of 2−300 K for both compounds. Measurements were performed on 5.88 mg of compound (**1**) at 10 kOe and 6.39 mg of compound (**2**) at 1 kOe using a Quantum Design SQUID magnetometer (MPMS-XL7).

3. Results and Discussion

3.1. X-ray Diffraction. The asymmetric unit of compound **1** is shown in Figure 1a. The copper atoms are in a square pyramidal environment: two nitrogen atoms from phenantroline ($d_{Cu-N} = 1.992-2.013$ Å) and two oxygen atoms from the same diphosphonic ligand ($d_{Cu-O} = 1.934-1.981$ Å) form the basal plane, and the apical position is occupied by an oxygen atom (water molecule for Cu1 and one oxygen atom from another diphosphonic ligand for Cu2) ($d_{Cu-Ow} = 2.247$ Å and $d_{Cu-O} = 2.280$ Å). The vanadium atoms are tetrahedraly coordinated with two terminal oxygen atoms ($d_{V-O} = 1.606-1.621$ Å), one oxygen atom shared with a diphosphonic group ($d_{V-O} = 1.866$ and 1.872 Å) and the other oxygen atom shared by two vanadium atoms forming $[V_2O_7]^{4-}$ entities ($d_{V-O} = 1.791$ and 1.798 Å, respectively). The methylene diphosphonic ligands share all their oxygen atoms: four of them with two copper atoms ($d_{P-O} = 1.501-1.518$ Å) and the other two, each with one vanadium atom, respectively ($d_{P-O} = 1.535$ and 1.545 Å).

The vanadium tetrahedra and the diphosphonate groups share common corners to form infinite zigzag chains $[(V_2O_5O_3PCH_2PO_3]$ running along the [100] direction. Edge-sharing of CuN_2O_3 tetragonal pyramids involving μ_3-oxo links results in dinuclear copper species with Cu−Cu distances as short as 3.25 Å. In turn, two copper atoms are linked to the dimer through two phosphonate groups to form tetranuclear copper units with longer Cu−Cu distances of 5.13 Å (Figure 2). The infinite chains are connected by the tetrameric units to

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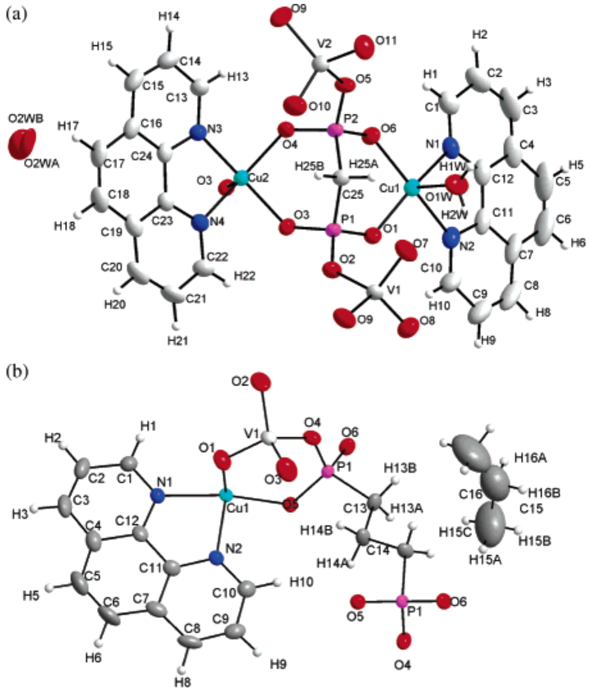

Figure 1. Asymmetric unit for (a) compounds **1** and (b) **2**.

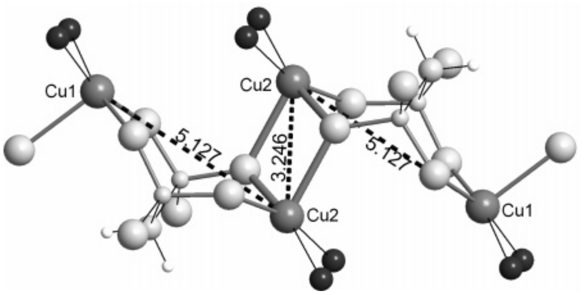

Figure 2. Tetranuclear copper species with the central bis-$\mu_3$oxo-bridge and the two external copper atoms bisphosphato-bridged with central copper atoms in compound **1**.

form layers. The layer shows 18-membered windows of approximately 13 × 13 Å^2 formed by 8 vanadium tetrahedra, 8 phosphorus tetrahedra, and 2 copper pyramids (Figure 3a).

Two different phenantroline groups are observed in the structure resulting in two ways of $\pi-\pi$ stacking. The first phenantroline group, connected to the copper atoms (2 × Cu2) of the dinuclear species, interact with the same type of adjacent layer. The second one, linked to the other copper atoms (2 × Cu1) of the tetranuclear group, interpenetrate the 18-membered rings of adjacent layers resulting in $\pi-\pi$ stacking with the same type of phenantroline groups in a third layer. This leads to a layered compound with water molecules occupying the interlamellar space (Figure 4a).

The asymmetric unit of (**2**) is represented in Figure 1b. The coordination around copper is defined by two nitrogen atoms from the phenantroline ligand (d_{Cu-N} = 2.005 and 2.029 Å) and two oxygen atoms (d_{Cu-O} = 1.905 Å and d_{Cu-O} = 1.926 Å) from the diphosphonate ligand, which form the basal plane of the square pyramid, while the oxygen atom in the apical position is only weakly bonded (d_{Cu-O} = 2.432 Å) and shared with a neighboring vanadium atom. The propylene diphosphonate group shares all its oxygen atoms: four oxygen atoms are coordinated to four copper atoms (d_{P-O} = 1.501 Å and d_{P-O} = 1.511 Å), and an oxygen atom bridges two vanadium atoms (d_{P-O} = 1.556 Å). The vanadium atom exhibits a tetrahedral coordination with one oxygen atom from the diphosphonate group (d_{V-O} = 1.854 Å), another bridging the copper atom (d_{V-O} = 1.640 Å), and a third terminal oxo-group (d_{V-O} = 1.605 Å). The fourth oxygen atom is shared between two vanadium tetrahedra to form $\{V_2O_7\}$ groups (d_{V-O} = 1.777 Å).

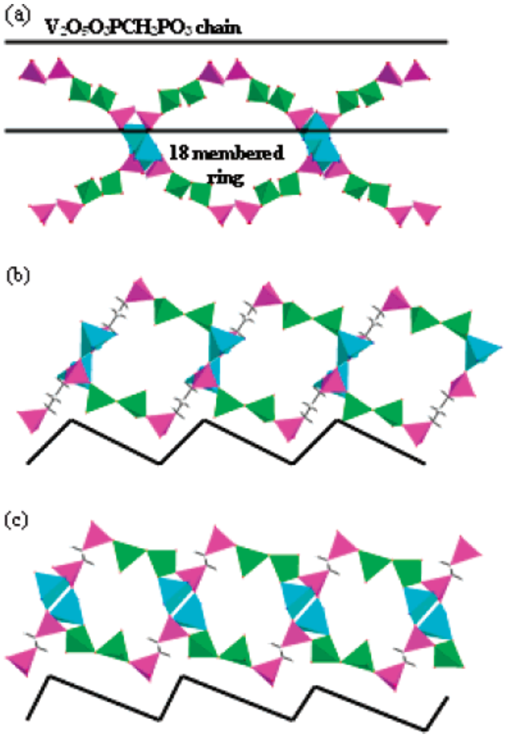

Figure 3. Comparison of the layer observed in (a) compound **1**, (b) compound **2**, and (c) $[(Cuphen)_2(O_3P(CH_2)_2PO_3)(V_2O_5)]$; the different $V_2O_5O_3P(CH_2)_xPO_3$ chains are emphasized. Green = vanadium, blue = copper, and purple = phosphorus.

The structure of (**2**) is built up of infinite chains of corner-sharing $\{V_2O_7\}$ groups and propylene diphosphonate ligands connected to each other by the copper atoms to form layers. The layer shows eight-membered windows of approximately 6 × 6 Å^2 formed by four vanadium tetrahedra, two copper pyramids, and two propylene diphosphonate ligands (Figure 3b). This window is quite similar to that observed in the compound $[(Cuphen)_2(O_3P(CH_2)_2PO_3)(V_2O_5)]$ (Figure 3c) previously described by Finn et al.,[34] the difference being caused by the further extension in the diphosphonate ligand.

The phenantroline groups connected to the copper atoms stack perpendicular to the layers. Zipperlike chains of two *phen* groups from one layer and two *phen* groups from the other layer are observed. The phenantrolines of two adjacent layers interdigitate resulting in a strong $\pi-\pi$ stacking of neighboring 1,10-phenantrolines (at a distance of approximately 3.4 Å). The layered character of the compound with alternating organic and inorganic layers is shown in Figure 4b.

One of the striking feature of compound (**2**) is the presence of propane molecules between the layers. The presence of such a molecule must have its origin in the decomposition

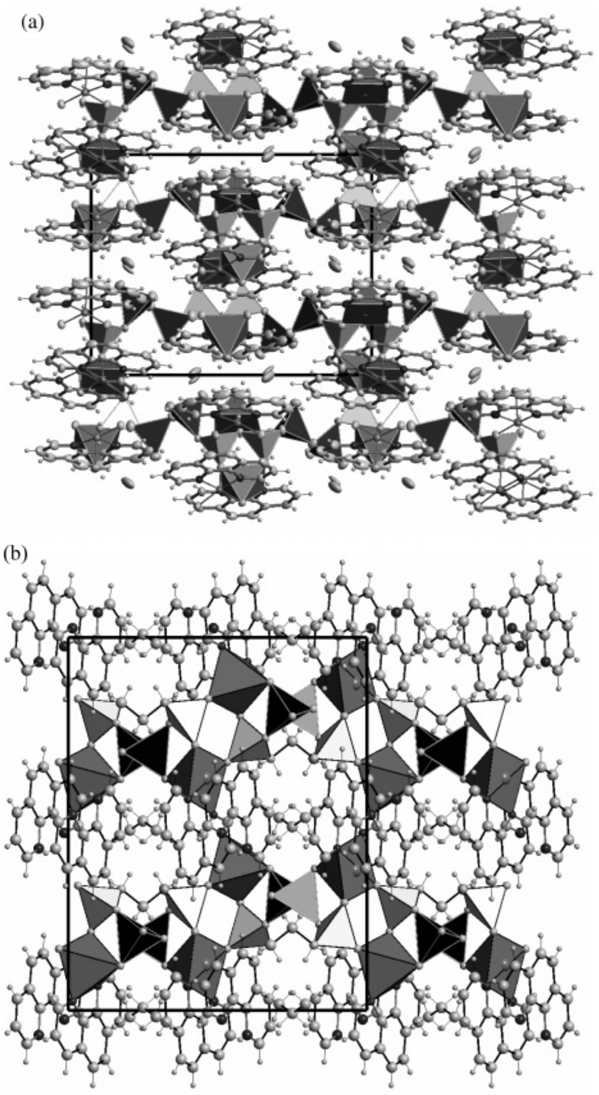

Figure 4. The structure of (a) [Cu_2 phen$_2$ ($O_3PCH_2PO_3$)(V_2O_5) (H_2O)]·H_2O and (b) [(Cuphen)$_2$($O_3P(CH_2)_3PO_3$)(V_2O_5)]·C_3H_8: view along [100]. Vanadium polyhedra are represented in black, copper polyhedra in gray, and PO_3C polyhedra in white.

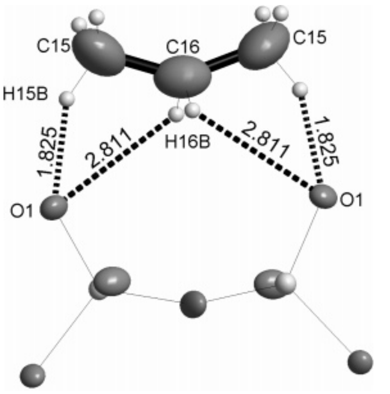

Figure 5. Hydrogen bonding between the propane molecule and the oxygen atoms of the {V_2O_7} unit.

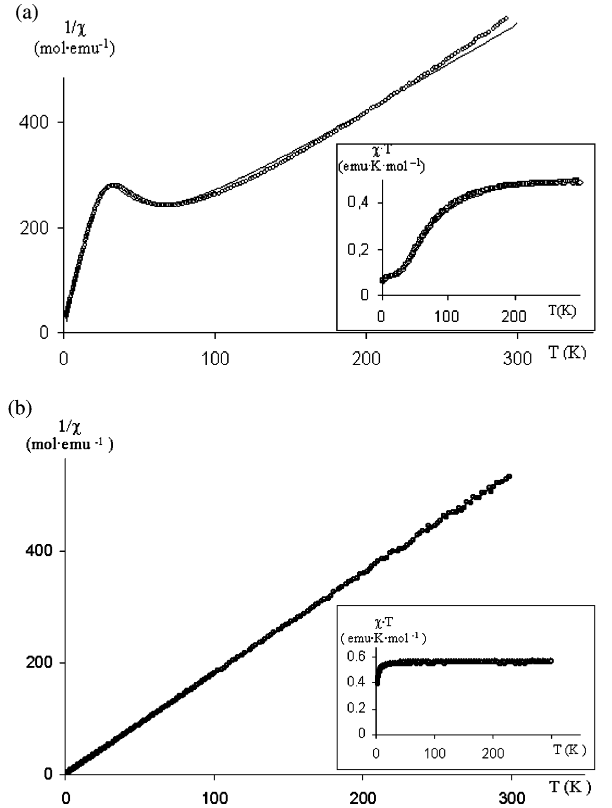

Figure 6. The χ^{-1} vs T curves (inset χT vs T) of (a) [Cu_2(phen)$_2$ ($O_3PCH_2PO_3$)(V_2O_5)(H_2O)]·H_2O (black circles represent the experimental data, and the continuous line represents the best fit using the tetrameric model in a field of $H = 10$ kOe) and (b) [Cu_2(phen)$_2$($O_3P(CH_2)_3PO_3$)(V_2O_5)]·C_3H_8 in a field of $H = 1$ kOe.

of the propylene diphosphonic acid used for the synthesis. As shown in Figure 5, short C−H···O distances are observed ($d_{C-H\cdots O} = 1.825$ Å), indicative of hydrogen bonding interactions with oxygen atoms from the vanadate groups, which allows the storage of such a molecule in this compound.

3.2. Magnetic Properties. The temperature dependence of the molar magnetic susceptibility/Cu(II) ion, χ_M, in the temperature range of 2−300 K is represented in Figure 6 for both compounds. After correction for TIP, the two compounds show Curie−Weiss behavior for the high-temperature region. Magnetic data gave magnetic moments per Cu of 2.11 μ_B ($\theta \approx -36.6$ K) and 2.11 μ_B ($\theta \approx -2$ K) for compounds (**1**) and (**2**), respectively. While two symmetric phosphato bridges between two copper centers, as in [Cu_2(phen)$_2$(H_2PO_4)$_2$](NO_3)$_2$·2H_2O, where the O−P−Cu angles are 135°, lead to antiferromagnetic dimers,[36] compound (**2**) shows an unexpected Curie−Weiss behavior in the whole range of temperature. This can be caused by an asymmetric Cu(II) dimeric unit in which the O−P−Cu angles are 129.3 and 145.4°. It is known that geometrical factors greatly influence the magnetic exchange coupling between the metal centers.

For compound (**1**), the magnetic behavior below 100 K is complex; the χ vs T curve shows a maximum at about 64 K, indicative of antiferromagnetic interactions, and a minimum at about 35 K. The magnetic data have been interpreted for compound (**1**) on the basis of structural results. The magnetic centers are the copper(II) species from the tetranuclear units with two central atoms with a short distance and two other copper atoms linked by the phosphonate groups to the central atoms. In a first step, considering that the prevailing magnetic interactions would occur in the central dimer, the molar magnetic susceptibility curve was fitted using the Bleaney−Bowers expression, corrected by monomeric impurities with Curie behavior [43] according to $\chi_{\mathrm{M}} = (1 - \rho)\chi_{\mathrm{dim.}} + \rho\chi_{\mathrm{mono.}}$ with $\chi_{\mathrm{dim.}} = 2Ng^2\beta^2[kT(3 + \exp(-J/kT)]^{-1}$ and $\chi_{\mathrm{mono.}} = Ng^2\beta^2S(S + 1)/(3kT)$, where N, g, β, and k have their usual meaning, J is the exchange coupling constant ,and ρ is the monomeric impurity fraction. The best fits were obtained for $J = -69.4$ K, $g = 1.69$, and $\rho = 0.15$. The g factor is quite small (even when considering the 15% of monomeric impurities) which is considered a signature of further interactions with the other copper atoms. As a consequence, a tetranuclear model has been then envisioned with two different pathways for the magnetic interaction: the first one between the two central $\mathrm{Cu^{II}}$ atoms with the corresponding exchange parameter, J_1, and the second one involving one external and one central $\mathrm{Cu^{II}}$ atom with the corresponding exchange parameter, J_2. The model previously described by Koval et al.[44] for the copper(II) compound $[\mathrm{Cu(CH_3COO)(CH_3O)}]n$, seemed appropriated and was used to fit the experimental data for compound (**1**). The expression of the susceptibility is given by $\chi = [(Ng^2\beta^2)/4k_{\mathrm{B}}T]\{[10\exp(-E_1/k_{\mathrm{B}}T) + 2\exp(-E_2/k_{\mathrm{B}}\mathrm{T}) + 2\exp(-E_3/k_{\mathrm{B}}T) + 2\exp(-E_4/k_{\mathrm{B}}T)]/[5\exp(-E_1/k_{\mathrm{B}}T) + 3\exp(-E_2/k_{\mathrm{B}}T) + 3\exp(-E_3/k_{\mathrm{B}}T) + 3\exp(-E_4/k_{\mathrm{B}}T) + \exp(-E_5/k_{\mathrm{B}}T) + \exp(-E_6/k_{\mathrm{B}}T)]\}$ using the low-lying energy levels: $E_1 = -(J_1 + J_2)$, $E_2 = J_1 - J_2$, $E_3 = J_2 - J_2$, $E_4 = J_1 + J_2$, $E_5 = J_1 + J_2 - 2(J_1^2 + J_2^2)^{1/2}$, and $E_6 = J_1 + J_2 + 2(J_1^2 + J_2^2)^{1/2}$. The best fit was obtained for $J_1 = -30$ cm^{-1}, $J_2 = -8.5$ cm^{-1}, and $g = 2.4$. This result clearly indicates that, as expected, the prevailing antiferromagnetic interactions occur between the two central copper atoms, while weakest antiferromagnetic interactions are observed with the bisphosphato-bridged copper. A paramagnetic impurity was introduced to fit the upturn of χ vs T at low temperature; 7.5% of impurity gives the most satisfying fit. This result is in good agreement with the extrapolated value ($\chi T \approx 0.08$ emu K mol^{-1}) of the χT curve at low temperature.

4. Conclusion

Two new hybrid organic/inorganic copper(II) oxovanadate(V) diphosphonates have been obtained from mild hydrothermal treatment. The two compounds present structural similarities: a two-dimensional framework and large ring apertures within the layers. The magnetic properties of $[\mathrm{Cu_2(phen)_2(O_3PCH_2PO_3)(V_2O_5)(H_2O)}]\cdot\mathrm{H_2O}$ have been successfully interpreted from structural results using a tetranuclear 1/2 spin model showing antiferromagnetic coupling between the copper centers. Propane molecules generated by the decomposition of the corresponding diphosphonate are stabilized in the structure of $[\mathrm{Cu_2(phen)_2(O_3P(CH_2)_3PO_3)(V_2O_5)}]$ $\mathrm{C_3H_8}$ by hydrogen bonding interactions.

Acknowledgment. The authors acknowledge the financial support of FONDAP (Grant 11980002), ECOS/CONICYT program C02E01. They are also grateful to Fundacion Andes for supporting the purchase of the SMART APEX system currently operating at the University of Chile. The authors want to thank Prof. M. T. Garland and A. Ibañez for the X-ray intensity data collection. S.U. thanks DAAD for a doctoral scholarship.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060152G

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